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(86) Silver-filled electrically conductive organosiloxane compositions.

(87) The electrical properties, particularly contact resistance and volume resistivity, of materials prepared by curing organosiloxane compositions containing finely divided silver as the electroconductive filler surprisingly enhanced by treating the silver particles with an organosilicon compound before incorporating the particles into said compositions.

This invention relates to storage-stable, silver-filled organosiloxane compositions yielding cured electrically conductive elastomers that retain their electrical properties for extended periods of time. The reduced variation of contact resistance and volume resistivity with time exhibited by our elastomers are attributed to the manner in which the silver particles are processed before incorporation into our curable organosiloxane composition.

Elastomers, gels and resins prepared from curable organosiloxane compositions containing finely divided silver particles exhibit high levels of electrical conductivity and are used in specialized applications that require materials exhibiting heat resistance, flex resistance, and electrical conductivity.

The prior art of electrically-conductive, silicone compositions is represented by JP-A 3-170,581 [170,581/91]; JP-A 03-049,105 [049,105/91]; JP-A 59-170,167 [170,167/84]; and US-A 5,227,093.

Several problems are associated with the electrically conductive silicone rubber compositions taught in the publications mentioned. When silver in flake-form is particularly used as a filler, it has been found that during the storage of the composition, the silver flakes separate from the composition, and the composition curability declines with the passage of time. Ultimately, the composition may even become uncureable.

Another problem is that large variations in contact resistance and volume resistivity can occur over time in the cured elastomers prepared from these compositions. This phenomenon can render the rubber unsuitable in use for the continuous connection of electrically conductive elements.

We have now found that one cause of variation in electrical properties of silver-filled organosiloxane elastomers with time is the low affinity of silver particles for the other ingredients of the curable composition used to prepare the elastomer.

We have also confirmed that the curability of these silicone rubber compositions declines with elapsed time due to the presence of residues of the lubricant which is present during grinding of the silver particles. These lubricant residues remain on the surface and/or in the interior of the particles.

One or more of the following lubricants are used with silver particles during this grinding: saturated and unsaturated higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, arachidic acid, and behenic acid; metal soaps such as aluminum laurate, aluminum stearate, zinc laurate, and zinc stearate; higher aliphatic alcohols such as stearyl alcohol; the esters of higher aliphatic alcohols and carboxylic acids; higher aliphatic amines such as stearylamine; higher aliphatic amides; and polyethylene waxes.

Initially, we attempted to remove the lubricant on the surface of the silver particles by subjecting the silver particles to repeated washings with organic solvents. These washings did not provide a satisfactory suppression of the timewise variation in the curability of electrically conductive silicone rubber compositions containing silver particles as a conductive filler.

We have also confirmed that a decline in adhesion and affinity between the cured elastomer and the silver particles contribute to timewise variations in, respectively, the contact resistance and volume resistivity of electrically conductive silicone rubbers.

As a result of our investigations directed at solving the above problems, we have found that the timewise variation in curability can be suppressed by treating silver particles with an organosilicon compound prior to combining said particles with the other ingredients of our curable organosiloxane composition.

We have further found that the presence in our curable compositions of an organosilicon compound containing silicon-bonded alkoxy groups, in addition to the compound used to treat the silver particles, further reduces timewise variations in contact resistance and volume resistivity of the cured elastomer.

The initial aspect of the present invention is achieved by first pretreating the silver particles intended for use in our organosiloxane compositions with an organosilicon compound before the particle is combined with the other ingredients of our compositions.

The variation in electrical properties with time exhibited by our curable composition is surprisingly reduced by the presence in the curable composition of an alkoxy-containing organosilicon compound as an additive. This compound is in addition to any used as the organosilicon compound for treatment of the silver particles. Alternatively, organohydrogensiloxane containing alkoxy groups may function both as the additive and the curing agent for our organosiloxane composition. An organohydrogensiloxane and an organosilicon compound containing silicon-bonded alkoxy groups may also be employed as separate ingredients.

The present invention provides an electrically conductive silicone rubber composition comprising
 (A) 100 parts by weight of a polyorganosiloxane containing at least two alkanyl radicals per molecule,
 (B) an organohydrogensiloxane containing at least two silicon-bonded hydrogen atoms in each molecule, in a quantity sufficient to provide from 0.5 to 3 silicon-bonded hydrogen atoms per alkanyl radical present in said polyorganosiloxane.

(C) from 50 to 2,000 parts by weight of finely divided silver particles treated with a first organosilicon compound selected from the group consisting of silanes containing at least one alkoxy group and organosiloxanes; and

(D) from one to 1,000 parts of a platinum group metal per one million parts of the combined weight of (A) and (B) of a hydrosilation catalyst to promote curing of said composition.

In our claimed invention, the silver particles are treated with an organosilicon compound selected from alkoxy silanes and organosiloxanes before combination with the other ingredients of our curable composition.

The variation in electrical properties with time of any cured materials prepared using our curable compositions can be reduced if the compositions contain up to 20 parts by weight of an organosilicon compound containing silicon-bonded alkoxy groups.

The characterizing feature of our curable organosiloxane compositions is the presence therein of silver particles that has been treated with an organosilicon compound before combination with the other ingredients of said composition.

The organosilicon compound, ingredient C, used to treat the silver particles is responsible for the enhanced electrical conductivity exhibited by the silicone rubbers prepared by curing our claimed compositions, irrespective of the storage time of said composition before its use.

The silver particles are prepared by the chemical or electrolytic reduction of a silver compound such as silver nitrate, or by atomization of molten silver. The silver particles to be treated in accordance with the present invention can be 100 percent pure silver or a silver alloy. Useful silver alloys include silver/copper alloys and silver/palladium alloys. The silver alloys may also contain trace amounts of other metals such as zinc, tin, magnesium, and nickel.

With respect to non-metallic impurities on the surface of the treated particles, the organosiloxane composition to avoid cure inhibition of it is particularly preferred that the NH_4^{+2} content not exceed 10 ppm and that the SO_4^{-2} content not exceed 5 ppm.

While no specific restrictions apply to the diameter of the silver, average particle diameters in the range of from 0.1 to 10 micrometers are preferred. Because the morphology of ingredient C is likewise not critical, the particles can be in the form of granules, dendrites, flakes or the particles may be amorphous. Mixtures of silver particles exhibiting various morphologies can also be used. The flake form of silver is preferred for the preparation of highly electrically conductive cured silicone elastomers.

The organosilicon compound used to treat the surface of the silver particles is not specifically restricted. Examples of suitable treating agents include:

alkoxy silanes such as methyltrimethoxysilane, vinyltrimethoxysilane, 3-glycidioxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, trimethylethoxysilane, tetramethoxysilane, and tetraethoxysilane;

siloxane oligomers such as silanol-endblocked dimethylsiloxane oligomers, silanol-endblocked dimethylsiloxane/methylvinylsiloxane co-oligomers, silanol-endblocked methylvinylsiloxane oligomers, silanol-endblocked methylphenylsiloxane oligomers, 1,3,5,7-tetramethylcyclotetrasiloxane, and 1,3,5,7,9-pentamethylcyclopentasiloxane;

polyorganosiloxanes ranging from low-viscosity liquids to gums, including trimethylsiloxy-endblocked polydimethylsiloxanes, trimethylsiloxy-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, trimethylsiloxy-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, trimethylsiloxy-endblocked polymethylhydrogensiloxanes, trimethylsiloxy-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers, silanol-endblocked polydimethylsiloxanes, silanol-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, silanol-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, silanol-endblocked polymethylhydrogensiloxanes, silanol-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers, dimethylvinylsiloxy-endblocked polydimethylsiloxanes, dimethylvinylsiloxy-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, dimethylvinylsiloxy-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, dimethylhydrogensiloxy-endblocked polymethylhydrogensiloxanes, and dimethylhydrogensiloxy-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers; and

silicone resins, including resins composed of $\text{R}_3\text{SiO}_{1.2}$ and $\text{SiO}_{4/2}$ units, silicone resins composed of $\text{RSiO}_{3/2}$ units, resins composed of the $\text{R}_2\text{SiO}_{2/2}$ and $\text{RSiO}_{3/2}$ units, and resins composed of the $\text{R}_2\text{SiO}_{3/2}$, $\text{RSiO}_{3/2}$, and $\text{SiO}_{4/2}$ units.

The organosilicon compounds used to treat the silver particles can be used singly or as mixtures of two or more compounds. The group represented by R in the units of the silicone resins represents any of the substituted and unsubstituted monovalent hydrocarbons discussed in this specification relating to the alkenyl-containing polyorganosiloxanes; used as ingredient A.

Silicone resins used as silver treating agents in our invention are preferably solids that soften at above room temperature, most preferably within the range from 50°C to 150°C.

The thickness of the coating of the organosilicon compound or a polycondensation product of this compound that is formed during treatment of the silver particles is not critical. The conductivity of cured silicone elastomers prepared from our filled silicone rubber compositions is typically inversely proportional to the thickness of the coating. However, thinner films reduce the affinity between the treated silver particles and the other ingredients of our curable organosiloxane compositions, resulting in larger decreases with the passage of time in the curability of these compositions.

For these reasons, while the optimal coating thickness will be dependent upon the particular end-use application, thicknesses not exceeding 0.1 micrometer are preferred. In order to obtain highly electrically conductive cured silicone rubber, the excess organosilicon compound, or the polycondensation products of this compound, should be removed from the surface of the silver particles by washing the particles with a suitable organic solvent.

The method for treating the silver particles with the organosilicon compound is not critical. As an example, the surface of the silver particles can be wetted with the compound in the absence of any solvent or with a solution of a liquid or solid organosilicon compound in a suitable organic liquid.

Our present treatment method is suitable for silver particles prepared by chemical reduction, electrolytic reduction, atomization, or by other means for the preparation of finely divided particles from molten silver and its alloys.

Chemically reduced silver particles can be prepared, by the reduction of an aqueous silver nitrate solution with a chemical reducing agent such as hydrazine, formaldehyde, or ascorbic acid.

Electrolytically reduced silver, in the form of dendrites, can be deposited on a cathode during the electrolysis of an aqueous silver nitrate solution.

Atomized silver particles can be prepared by spraying molten silver heated to at least 1,000°C into either water or inert gas.

No specific restrictions apply to the technique for wetting the silver particles with the neat organosilicon compound or solutions of that compound in a suitable organic liquid. Suitable treatment techniques include spraying the silver particles with a neat or solubilized organosilicon compound, immersing the silver particles in a neat or solubilized organosilicon compound, and grinding the silver particles using the neat or solubilized organosilicon compound as a lubricant.

Methods involving grinding are preferred because they produce a flake form of silver that is particularly suitable for preparing highly electrically conductive silicone rubber. The grinding process yields particularly desirable results for the silver flake product. During the grinding of silver particles, the organosilicon compound functions as a surface-treatment agent, and accelerates flake formation by becoming adsorbed onto the activated surface of the flakes. Thus, the aggregation of flakes into larger particles is inhibited.

The device for grinding the silver particles is not critical. Useful devices for this purpose are stamping mills, ball mills, vibratory mills, hammer mills, roll mills, and a mortar and pestle.

The conditions for milling the silver particles are not specifically restricted. They will be dependent at least in part on the diameter and shape of the silver particles. Grinding is preferably conducted while cooling the grinder due to the heat generated during this operation. The silver particles produced by grinding are in the form of flakes that preferably have a diameter in the range of from 0.1 to 10 micrometers.

To facilitate formation of the desired thin coating of the organosilicon compound on the silver particles or when the compound has a relatively high viscosity, the compound(s) used to treat the particles is preferably dissolved in a suitable organic liquid. No specific restrictions apply to organic solvents usable for this purpose. Suitable solvents include alcohols such as methanol, ethanol, and isopropanol; aliphatic compounds such as hexane, heptane, and octane; alicyclic compounds such as cyclohexane and cyclooctane; aromatic compounds toluene and xylene; ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; and esters such as ethyl acetate, and Carbitol™ acetate.

No specific restrictions apply to the conditions for treating the surface of the silver particles with the organosilicon compound during the preparation of ingredient C. Treatment of the particles is preferably carried out at temperatures from ambient to 100°C, preferably at least 50°C, for periods from 24 to 150 hours.

To facilitate drying and to also remove excess organosilicon compound adhering to the silver particles, the treated silver particles are preferably washed with a suitable organic solvent, and is then dried for at least 24 hours at temperatures from ambient to 105°C.

The concentration of the treated silver particles (ingredient C) in the claimed compositions is typically from 50 to 2,000 parts by weight, preferably from 300 to 600 parts, per 100 parts by weight of the

polyorganosiloxane of ingredient A. When the concentration of ingredient C is less than 50 parts per 100 parts of ingredient A, there is a substantial decline in the electrical conductivity of our cured silicone rubber product.

- 5 When ingredient C exceeds 2,000 weight parts per 100 weight parts of ingredient A, there is typically a substantial decline in the fluidity of the corresponding composition and the ability to process the composition becomes very problematic.

The alkenyl-substituted polyorganosiloxane of ingredient A is essential to the present curable compositions. This ingredient contains at least 2 alkenyl radicals in each molecule. Suitable alkenyl radicals are vinyl, allyl, butenyl, pentenyl, hexenyl, and heptenyl, with vinyl being preferred. The location of the alkenyl
10 radicals in ingredient A can be at the molecular chain terminals, on non-terminal silicon atoms, or at both positions.

No specific restrictions apply to the silicon-bonded organic groups other than alkenyl radicals. These groups are substituted or unsubstituted monovalent hydrocarbon radicals like alkyl such as methyl, ethyl, propyl, butyl, pentyl and hexyl; aryl such as phenyl, tolyl and xylyl; aralkyl such as benzyl and phenethyl;
15 and haloalkyl such as 3-chloropropyl and 3,3,3-trifluoropropyl. Of these radicals, methyl and phenyl are preferred.

The molecular structure of ingredient A is also not critical and is exemplified by straight chains, partially branched straight chains, branched chains, and network type resin structures. Straight-chain and partially branched straight-chain structures are preferred.

- 20 The viscosity of ingredient A is not critical. Typical polymers exhibit viscosity values, measured at 25 °C, in the range from 50 to 500,000 centipoise (0.05 to 500 Pa.s) while particularly preferred values fall in the range of from 400 to 100,000 centipoise (0.4 to 100 Pa.s)

Specific polyorganosiloxanes suitable for use as Ingredient A are trimethylsiloxy- endblocked dimethylsiloxane/methylvinylsiloxane copolymers, trimethylsiloxy-endblocked polymethylvinylsiloxanes, trimethylsiloxy-endblocked methylvinylsiloxane/methylphenylsiloxane copolymers, trimethylsiloxy-endblocked dimethylsiloxane/methylvinylsiloxane/methylphenylsiloxane copolymers, dimethylvinylsiloxy-endblocked polydimethylsiloxanes, dimethylvinylsiloxy-endblocked polymethylvinylsiloxanes, dimethylvinylsiloxy-endblocked polymethylphenylsiloxanes, dimethylvinylsiloxy-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, dimethylvinylsiloxy-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, silanol-endblocked dimethylsiloxane/methylvinylsiloxane copolymers, silanol-endblocked dimethylsiloxane/methylvinylsiloxane/methylphenylsiloxane copolymers.
30 and silanol-endblocked dimethylsiloxane/methylvinylsiloxane copolymers.

Alkenyl-substituted organosiloxane resins suitable for use as ingredient A include resins composed of the combination $R_3SiO_{1/2}$ and $SiO_{4/2}$ units, the $RSiO_{3/2}$ unit alone, the combination of R_2SiO and $RSiO_{3/2}$ units, the combination of R_2SiO , $RSiO_{3/2}$ and $SiO_{4/2}$ units, and mixtures containing two or more of these resins.
35

The monovalent hydrocarbon radicals represented by R are substituted or unsubstituted, and include alkyl such as methyl, ethyl, propyl, butyl, pentyl and octyl; alkenyl such as vinyl, allyl, butenyl, pentenyl and hexenyl; aryl such as phenyl, tolyl and xylyl, and haloalkyl such as 3-chloropropyl and 3,3,3-trifluoropropyl. The only proviso is that at least one of the R groups represents an alkenyl radical.

- 40 The organohydrogensiloxanes referred to as ingredients B and B' function as crosslinkers that are responsible for curing the present compositions. The organohydrogensiloxane should contain at least 2 silicon-bonded hydrogen atoms in each molecule. The location of these silicon-bonded hydrogen atoms is not critical, and they may be located, at the molecular chain terminals, on non-terminal silicon atoms, or at both positions.

45 No specific restrictions apply to the silicon-bonded organic groups in ingredient B, which are substituted and unsubstituted monovalent hydrocarbon radicals, and which are the same for ingredient A, with the exception that alkenyl and other ethylenically unsaturated radicals are excluded.

The molecular structure of ingredient B is likewise not critical and is straight chain, partially branched straight chain, branched, and network. Straight-chain and partially branched straight-chain structures are preferred.
50

The viscosity of ingredient B is not critical, however preferred viscosity values measured at 25 °C are in the range of from 1 to 50,000 centipoise, (0.001 to 50 Pa.s), with particularly preferred values being in the range of 5 to 1,000 centipoise (0.005 to 1 Pa.s).

- 55 Examples of suitable organohydrogensiloxanes are trimethylsiloxy-endblocked polymethylhydrogensiloxanes, trimethylsiloxy-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers, trimethylsiloxy-endblocked methylhydrogensiloxane/methylphenylsiloxane copolymers, trimethylsiloxy-endblocked dimethylsiloxane/methylhydrogensiloxane/methylphenylsiloxane copolymers, dimethylhydrogensiloxy-endblocked polydimethylsiloxanes, dimethylhydrogensiloxy-endblocked polymethylhydrogensiloxanes,

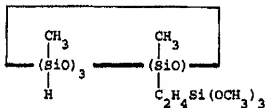
dimethylhydrogensiloxy-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers, dimethylhydrogensiloxy-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, dimethylhydrogensiloxy-endblocked polymethylphenylsiloxanes, silanol-endblocked polymethylhydrogensiloxanes, silanol-endblocked dimethylsiloxane/methylhydrogensiloxane copolymers, and silanol-endblocked dimethylsiloxane/methylphenylsiloxane copolymers, and silanol-endblocked dimethylsiloxane/methylhydrogensiloxane/methylphenylsiloxane copolymers.

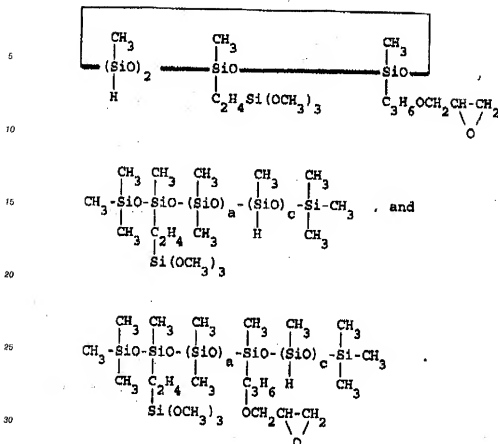
In an alternative embodiment of the invention, ingredient B' functions both as an adhesion promoter and as a crosslinker for the curable composition. Each molecule of ingredient B' must contain at least 2 silicon-bonded hydrogen atoms and at least 1 silicon-bonded alkoxy group. The location of the silicon-bonded hydrogen atoms in ingredient B' is not critical. They may be bonded to terminal or non-terminal silicon atoms, or at both of these positions. The bonding position for the silicon-bonded alkoxy groups in ingredient B' is also not critical, and this group may be bonded to terminal and/or non-terminal silicon atoms.

The silicon-bonded organic groups that are present in ingredient B' are free of ethylenic unsaturation and are exemplified by the monovalent substituted and unsubstituted hydrocarbon radicals of ingredient B. Ingredient B' can contain other adhesion-promoting groups that will not interfere with curing of the present compositions. These additional adhesion-promoting groups include epoxy groups that are bonded to a silicon atom by means of a carbon atom that is not a part of the epoxide ring.

The molecular structure of ingredient B' straight chains, partially branched straight chains, branched chains, cyclic and network structures. Mixtures of polyorganosiloxanes having two or more types of structures can also be used. While the viscosity of ingredient B' is not critical, viscosities of from 1 to 50,000 centipoise (0.001 to 50 Pa.s), measured at 25° C, are preferred, the range from of 5 to 1,000 centipoise (0.005 to 1 Pa.s) being particularly preferred.

Polyorganosiloxanes suitable for use as ingredient B' include:





In these formulae, a represents an integer with a value of at least 1, and c represents an integer with a value of at least 2.

No particular restrictions apply to the method for preparing ingredient B'. Suitable methods are:

- (a) the platinum-catalyzed addition of an alkenyl-containing alkoxysilane to a portion of the silicon-bonded hydrogen atoms of an organohydrogensiloxane containing at least 3 silicon-bonded hydrogen atoms in each molecule, and
- (b) the platinum-catalyzed addition of an alkenyltrialkoxysilane and an alkenyl-containing epoxy compound to a portion of the silicon-bonded hydrogen atoms of an organohydrogensiloxane containing at least 4 silicon-bonded hydrogen atoms in each molecule.

Platinum catalysts useful for preparing ingredient B' include the same catalysts described as ingredient D. Polyorganosiloxanes containing at least three or four silicon-bonded hydrogen atoms and suitable for use in preparing ingredient B' include trimethylsiloxy-endblocked polymethylhydrogensiloxanes, trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylhydrogensiloxy-endblocked polymethylhydrogensiloxanes, dimethylhydrogensiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers, cyclic methylhydrogensiloxanes, and cyclic dimethylsiloxane-methylhydrogensiloxane copolymers.

Alkenyl-containing alkoxysilanes suitable for use in preparing ingredient B' include vinyltrimethoxysilane, vinyltriethoxysilane, vinylmethyldimethoxysilane, vinyldimethylmethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, allylmethyldimethoxysilane, allyldimethylmethoxysilane, and butenyltrimethoxysilane.

Alkenyl-containing epoxy compounds suitable for use in preparing ingredient B' are vinyl glycidyl ether, allyl glycidyl ether, butenyl glycidyl ether, 3,4-epoxycyclohexylethene, 3-(3,4-epoxycyclohexyl)propene, and 4-(3,4-epoxycyclohexyl)butene.

Because ingredient B' must contain at least two silicon bonded hydrogen atoms per molecule, the total number of moles of alkenyl-containing alkoxysilane and alkenyl-containing epoxy compound used to prepare this ingredient must be at least two less than the number of moles of silicon-bonded hydrogen

present in the initial organohydrogensiloxane.

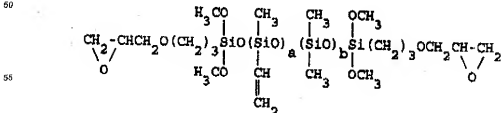
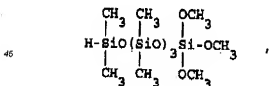
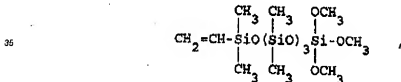
The concentration of ingredients B and B' in the present compositions is sufficient to provide from 0.5 to 3 silicon-bonded hydrogen atoms per alkenyl group in ingredient A. The composition will not cure adequately when ingredients B and B' provide fewer than 0.5 silicon-bonded hydrogen atoms per alkenyl radical. At the other extreme, the presence in the curable composition of more than 3 silicon-bonded hydrogen atoms per alkenyl group yields a cured electrically conductive silicone rubber with a drastically reduced heat resistance.

The platinum containing hydrosilation catalyst, ingredient D, accelerates the cure of our compositions. Any metal from the platinum group of the periodic table capable of functioning as catalysts for hydrosilation reactions can be used as ingredient D. Suitable catalysts include platinum black, platinum supported on powdered alumina, platinum supported on powdered silica, platinum supported on powdered carbon, chloroplatinic acid, alcohol solutions of chloroplatinic acid, chloroplatinic acid/olefin complexes, chloroplatinic acid/vinylsiloxane complexes, and platinum catalysts dispersed in microparticulate forms of thermoplastic organic resins such as methyl methacrylate resins, polycarbonate resins, polystyrene resins, and silicone resins.

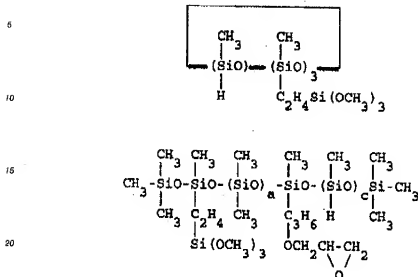
The concentration of ingredient D in the present compositions is typically not critical so long as it is sufficient to promote curing of the composition, and is typically equivalent to from 1 to 100 ppm of platinum metal, based on the combined weights of ingredients A and B.

Curable compositions of the present invention typically contain only ingredients A - D. However, an organosilicon compound containing at least one silicon-bonded alkoxy group per molecule, optional ingredients E and E', is preferably included in our compositions to diminish timewise variations in contact resistance and volume resistivity values exhibited by the cured materials prepared from these compositions. Ingredient E is used when ingredient B is employed as the organohydrogensiloxane, and ingredient E' is used in combination with ingredient B'.

Examples of suitable organosilicon compounds for ingredient E are alkoxyxilanes such as tetramethoxyxilane, tetraethoxyxilane, dimethyldimethoxyxilane, methylphenyldimethoxyxilane, methylphenyldiethoxyxilane, phenyltrimethoxyxilane, methyltrimethoxyxilane, methyltriethoxyxilane, vinyltrimethoxyxilane, allyltrimethoxyxilane, allyltriethoxyxilane, 3-glycidyloxypropyltrimethoxyxilane, 3-methacryloxypropyltrimethoxyxilane, and organosilicon compounds with the following formulae:



wherein a and b are each integers with values of at least 1



where a is an integer with a value of at least 1 and c is 0 or 1.

Ingredient E' is an organosilicon compound that contains silicon-bonded alkoxy groups and either one or no silicon-bonded hydrogen. Ingredient E' can be any of the organosilicon compounds suitable for use as ingredient E that contain a maximum of one silicon-bonded hydrogen atom.

When they are present, the concentrations of ingredients E and E' are up to 20 weight percent, based on the weight of ingredient A, preferably from 0.5 to 8 weight percent. The appearance of timewise variations in the contact resistance and volume resistivity values of the cured elastomer becomes a possibility when ingredient E or E' is not present. On the other hand, the addition of more than 20 weight percent of ingredient E or E' based on ingredient A results in a decline in the storage stability of the resulting composition and also in an increase in the hardness of the cured elastomer with elapsed time.

A cure inhibitor may also be added to the claimed composition as an optional ingredient to improve the storage stability and handling characteristics of our curable composition. Suitable cure inhibitors are alkynyl alcohols such as 3-methyl-1-butyne-3-ol, 3,5-dimethyl-1-hexyne-3-ol and phenylbutynol; ene-yne compounds such as 3-methyl-3-penten-1-yne and 3,5-dimethyl-3-hexen-1-yne; and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane, and benzotriazole.

These cure inhibitors are preferably added at 0.001 to 5 weight parts per 100 weight parts of ingredient A.

The present curable compositions can also include an inorganic filler to impart a suitable hardness and strength to the cured elastomer. Suitable inorganic fillers are fumed silica, crystalline silica, calcined silica, wet-process silica, fumed titanium oxide, and carbon black, and inorganic filler whose surface has been treated with an organosilicon compound such as an organoalkoxysilane, organochlorosilane or an organodisilazane.

These inorganic fillers are preferably added at no more than 50 weight parts per 100 weight parts of ingredient A.

The elastomers prepared using our curable organosiloxane compositions typically exhibit volume resistivities below 0.1 ohm-cm, preferably below 1×10^{-3} ohm-cm, and are useful as electrically conductive adhesives, electrically conductive die-bonding agents, as heat-dissipating die-bonding agents, and as electromagnetic-shielding agents.

The following examples describe preferred compositions of the present invention and the electrically conducting elastomers prepared using our compositions. Unless otherwise specified all parts and percentages are by weight and reported viscosity values were measured at 25 °C.

The following methods were used to measure the properties of our curable organosiloxane compositions and the electrically conductive cured elastomers prepared therefrom.

Appearance of the electrically conductive silicone rubber compositions

The electrically conductive silicone rubber compositions were stored in transparent glass bottles that were maintained under refrigeration. The appearance of the composition was inspected immediately after preparation (initial evaluation) and following 1 month, 3 months, and 6 months of storage.

Curability of the compositions

The curable, electrically conductive compositions were stored under refrigeration after being prepared. Samples were taken from these compositions immediately following their preparation (initial evaluation) and after 1, 3, and 6 months. Cured elastomers were then prepared from these samples by heating them for 30 minutes at 150°C. The curability of the compositions was evaluated by measuring the hardness of the cured elastomers using a JIS A hardness meter in accordance with JIS K 6301.

Contact resistance of the silicone rubbers

Each of the curable compositions was coated on one surface of a circuit board and heated for 30 minutes at 150°C to produce a cured elastomer. The contact resistance of the silicone rubber was then measured using the "4-point method" to give the initial value. The contact resistance of the silicone rubber was measured by the same method after the elastomer-coated circuit board had been heated for 100 hours, 500 hours, and 1,000 hours in an oven maintained at 150°C.

Volume resistivity of the silicone rubbers

An electrically conductive elastomer in the form of a sheet with a thickness of at least 1 mm was prepared by heating the curable silver-filled organosiloxane compositions at 150°C for 30 minutes. The initial volume resistivity of this silicone rubber sheet was measured using a model K-705RL meter from Yugen Kaisha Kyowa Riken. In order to measure the timewise variation in the volume resistivity of the silicone rubber, the volume resistivity of each of the elastomer sheets was measured by the same method after the sheets had been held for 100 hours, 500 hours, and 1,000 hours in a 150°C oven.

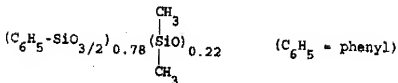
Adhesion of the cured elastomers

The adhesion of the electrically conductive silicone elastomers was measured using a tab bonding test. The evaluated curable compositions were first heated for 30 minutes at 150°C on an aluminum plate to form a silicone rubber bead measuring 20 mm in width, 20 mm in length and 5 mm in thickness. This cured elastomeric bead was then peeled from the aluminum plate, and the surface that had been in contact with the heated plate was examined. A rating of "CF" indicates the occurrence of cohesive failure within the body of the elastomer, thereby leaving the plate covered with some portion of the cured elastomer. A rating of "AF" refers to adhesive failure that occurred only at the interface between the elastomer and the aluminum plate surface. A rating of "partial AF" indicates only partial interfacial failure and some within the body of the cured elastomer. A score of "TCF" refers to the presence of a thin layer of silicone rubber adhering to the aluminum plate.

The evaluation results for curable compositions and elastomers of the present invention are recorded in Table 1 and the evaluation results for the comparative examples are recorded in Table 2.

Example 1

20 g of silver nitrate were dissolved in 40 mL water, from which granular silver oxide was subsequently precipitated by the addition of a 46% aqueous solution of sodium hydroxide. This granular silver oxide was chemically reduced with formalin, and the product was repeatedly washed and filtered to yield a granular form of reduced silver with an average particle diameter of 1 micrometer. The silver particles were then immersed in a Carbitol™ acetate solution of a dimethylsiloxane/phenylsiloxane resin exhibiting a softening point of 90°C and the average unit formula



Following surface treatment using methylphenylsiloxane resin, the silver particles were recovered on filter paper and then dried at room temperature to yield granular silver particles with an average particle diameter of 1 micrometer.

A curable organosiloxane composition of this invention was prepared by blending the following ingredients to homogeneity:

- 600 parts by weight of treated silver particles,
- 100 parts by weight of a dimethylvinylsiloxy-endblocked dimethylpolysiloxane with a viscosity of 2 Pa.s (2,000 centipoise) and a vinyl content of 0.2 weight percent,
- 1 part by weight of a trimethylsiloxy-endblocked methylhydrogen-polysiloxane exhibiting a viscosity of 0.03 Pa.s (30 centipoise) and containing 1.5 weight percent of silicon-bonded hydrogen,
- 7 parts by weight of 3-glycidoxypropyltrimethoxysilane,
- a quantity of a chloroplatinic acid/vinylsiloxane complex, equivalent to 5 ppm of complexed platinum metal in the composition, and
- 300 ppm, based on the weight of the curable composition, of phenylbutynol as a catalyst inhibitor.

The appearance and curability of the resultant curable composition were evaluated together with the adhesion, contact resistance and volume resistivity. The results of these evaluations are reported in Table 1.

Comparative Example 1

20 g silver nitrate were dissolved in 40 mL water, from which granular silver oxide was subsequently precipitated by the addition of 46% aqueous sodium hydroxide. This granular silver oxide was reduced with formalin, and the product was repeatedly washed and filtered to yield granular reduced silver particles with an average particle diameter of 1 micrometer.

A curable organosiloxane composition outside the scope of the claimed invention was prepared by mixing the types and amounts of ingredients described in Example 1 of this specification to homogeneity using these silver particles.

The appearance and curability of the resultant curable organosiloxane composition together with the adhesion, contact resistance and volume resistivity of the cured elastomer prepared from this composition were evaluated and the results are reported in Table 2.

Example 2

20 g silver nitrate were dissolved in 40 mL water, from which granular silver oxide was subsequently precipitated by the addition of 46% aqueous sodium hydroxide. This granular silver oxide was reduced with formalin, and the product was repeatedly washed and filtered to yield granular reduced silver particles with an average particle diameter of 1 micrometer. The particles were ground in a ball mill using Carbitol™ acetate solution of dimethylsiloxane/phenylsiloxane resin of Example 1 as a lubricant.

After surface treatment of the silver particles, the particles were washed with xylene to obtain washed flakes with an average particle diameter of 8 micrometers.

An electrically conductive silicone rubber composition was subsequently prepared by mixing the types and amounts of ingredients described in Example 1 of this specification to homogeneity using the silver particles prepared as described above.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer obtained by curing the composition were evaluated and the results are reported in Table 1.

Comparative Example 2

20 g silver nitrate were dissolved in 40 mL water, from which granular silver oxide was subsequently precipitated by the addition of 46% aqueous sodium hydroxide. This granular silver oxide was reduced with

formalin, and the product was repeatedly washed and filtered to yield granular reduced silver particles with an average particle diameter of 1 micrometer. The reduced silver particles were ground in a ball mill using a Carbitol™ acetate solution of stearic acid as a lubricant. Following surface treatment with stearic acid, the silver particles were washed with methanol to yield silver flake with an average particle diameter of 8 micrometers.

A curable organosiloxane composition outside the scope of the present invention was prepared by mixing the types and amounts of ingredients described in Example 1 of this specification to homogeneity using these silver particles.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 2.

Example 3

Granular silver particles prepared by atomization in water were ground in a ball mill using as the lubricant a xylene solution of a dimethylvinylsiloxy-*endblocked* polydimethylsiloxane exhibiting a viscosity 100 centipoise (0.1 Pa.s). Following this treatment, the silver particles were washed with xylene to yield silver flakes with an average particle diameter of 10 micrometers.

A curable organosiloxane composition of the present invention was prepared by blending the following ingredients to homogeneity:

- 980 weight parts of the silver flake,
- 100 parts by weight of a dimethylvinylsiloxy-*endblocked* dimethylpolysiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and a vinyl content of 0.2 weight percent,
- 1 part by weight of a trimethylsiloxy-*endblocked* polymethylhydrogensiloxane with a viscosity of 0.03 Pa.s (30 centipoise) and a silicon-bonded hydrogen content of 1.5 weight percent,
- 7 parts by weight of 3-glycidioxypropyltrimethoxysilane,
- a quantity of a chloroplatinic acid/vinylsiloxane complex sufficient to provide 5 ppm, based on the total weight of the curable composition, of complexed platinum metal in the composition, and
- 300 ppm, based on the weight of the curable composition, of phenylbutynol as the catalyst inhibitor.

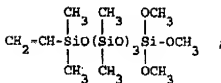
The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Example 4

20 g silver nitrate were dissolved in 40 mL water, from which granular silver oxide was subsequently precipitated by the addition of 46% aqueous sodium hydroxide. This granular silver oxide was reduced with formalin, and the product was repeatedly washed and filtered to yield granular reduced silver particles with an average diameter of 3 micrometers. These particles were ground in a ball mill using as lubricant the Carbitol™ acetate solution of a dimethylvinylsiloxy-*endblocked* dimethylpolysiloxane (viscosity = 0.1 Pa.s/100 centipoise). After its surface treatment with dimethylpolysiloxane, the silver particles were washed with Carbitol™ acetate to yield a silver flake with an average particle diameter of 4 micrometers.

A curable organosiloxane composition of the present invention was prepared by blending the following ingredients to homogeneity:

- 400 parts by weight of the silver flake,
- 100 parts by weight of mixture containing a) a dimethylvinylsiloxy-*endblocked* polydimethylsiloxane and b) an organosiloxane resin containing trimethylsiloxy, dimethylvinylsiloxy and SiO₄₂ units, the mixture exhibiting a viscosity of 8,000 centipoise (8 Pa.s) and a vinyl content of 0.8 weight percent;
- 5 parts by weight of a trimethylsiloxy-*endblocked* polymethyl-hydrogensiloxane with a viscosity of 30 centipoise (0.03 Pa.s) and a silicon-bonded hydrogen content of 1.5 weight percent,
- 10 parts by weight of an organosilicon compound with the formula



a quantity of a chloroplatinic acid/vinylsiloxane complex equivalent to 5 ppm of complexed platinum metal, based on the total weight of the curable composition, and

300 ppm, based on the total weight of the curable composition, of phenylbutynol as the catalyst inhibitor.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Comparative Example 3

20 g of silver nitrate were dissolved in 40 mL water, from which granular silver oxide was subsequently precipitated by the addition of 46% aqueous sodium hydroxide. This granular silver oxide was reduced with formalin, and the product was repeatedly washed and filtered to yield granular reduced silver particles with an average particle diameter of 3 micrometers. These reduced silver particles were ground in a ball mill using stearic acid as the lubricant. After its surface treatment with stearic acid, the silver particles were washed with xylene to yield particles in the form of flakes with an average particle diameter of 4 micrometers.

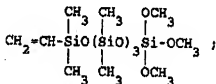
A curable organosiloxane composition outside the scope of the present invention was prepared by blending the following ingredients to homogeneity:

450 parts by weight of the silver flakes,

100 parts by weight of a mixture containing a) a dimethylvinylsiloxy-terminated polydimethylsiloxane and b) an organosiloxane resin containing trimethylsiloxy, dimethylvinylsiloxy and SiO_2 units, the mixture exhibiting a viscosity of 8,000 centipoise (8 Pa.s) and a vinyl content of 0.8 weight percent;

5 parts by weight of a trimethylsiloxy-terminated polymethylhydrogensiloxane with a silicon-bonded hydrogen content of 1.5 weight percent and a viscosity of .03 Pa.s (30 centipoise),

10 parts by weight of an organosilicon compound with the formula



a quantity of a chloroplatinic acid/vinylsiloxane complex equivalent to 5 ppm, based on the total weight of the curable composition, of complexed platinum metal in the composition, and

300 ppm, based on the total weight of the curable composition, of phenylbutynol as the catalyst inhibitor.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 2.

Example 5

20 g silver nitrate were dissolved in 40 mL water, from which granular silver oxide was subsequently precipitated by the addition of 46% aqueous sodium hydroxide. This granular silver oxide was reduced with formalin, and the product was repeatedly washed and filtered to yield granular reduced silver particles with an average particle diameter of 1 micrometer. These particles were ground in a ball mill using a methanol solution of vinyltrimethoxysilane as the lubricant. Following this treatment the silver particles were washed

with methanol to yield silver flake with an average particle diameter of 2 micrometers.

An electrically conductive silicone rubber composition according to the invention was subsequently prepared by mixing the following to homogeneity:

400 parts by weight of the silver particles,

100 parts by weight of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and a vinyl content of 0.2 weight percent,

1 weight part trimethylsiloxy-endblocked polymethylhydrogensiloxane with a viscosity of 30 centipoise (0.03 Pa.s) and a silicon-bonded hydrogen content of 1.5 weight percent,

7 parts by weight of 3-glycidyloxypropyltrimethoxysilane,

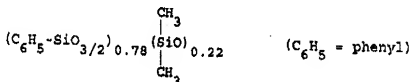
a quantity of a chloroplatinic acid/vinylsiloxane complex equivalent to 5 ppm, based on the total weight of the curable composition, of complexed platinum metal in the composition, and

300 ppm, based on the total weight of the curable composition, of phenylbutynol as the catalyst inhibitor.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Example 6

Dendritic electrolytic silver particles with an average particle diameter of 10 micrometers were ground in a ball mill using as the lubricant a Carbitol™ acetate solution of a dimethylsiloxane/phenylsiloxane resin exhibiting a softening point of 90°C and the average unit formula.



Following this surface treatment the silver particles were washed with xylene to yield silver flake with an average particle diameter of 12 micrometers.

A curable composition of this invention was prepared by blending the following ingredients to homogeneity:

400 parts by weight of the silver particles

100 parts of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and a vinyl content of 0.2 weight percent,

1 part by weight of a trimethylsiloxy-endblocked polymethylhydrogensiloxane with a viscosity of 30 centipoise (0.03 Pa.s) and a silicon-bonded hydrogen content of 1.5 weight percent,

7 parts by weight of 3-glycidyloxypropyltrimethoxysilane, a quantity of a chloroplatinic acid/vinylsiloxane complex equivalent to 5 ppm, based on the total weight of the curable composition, of complexed platinum metal, and

300 ppm, based on the total weight of the curable composition, of phenylbutynol as a catalyst inhibitor.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Example 7

100 g reduced silver particles in flake form with an average particle diameter 4 micrometers were placed in a flask, followed by the addition of 170 g heptane, 0.5 g tetrabutyl titanate, and 5 g trimethylmethoxysilane. After stirring at room temperature for 4 hours the silver particles were isolated by filtration. The treated particles were washed with methanol and then dried at 35°C for 48 hours to yield silver flake with an average particle diameter of 4 micrometers.

A curable organosiloxane composition of this invention was prepared by blending the following ingredients to homogeneity:

400 parts by weight of the silver particles

100 weight parts dimethylvinylsiloxo-endblocked polydimethylsiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and a vinyl content of 0.2 weight percent,

1 part by weight of a trimethylsiloxo-endblocked polymethylhydrogensiloxane with a viscosity of 0.03 Pa.s (30 centipoise) and a silicon-bonded hydrogen content of 1.5 weight percent,

- 5 7 parts by weight of 3-glycidyloxypropyltrimethoxysilane, a quantity of a chloroplatinic acid/olefin complex equivalent to 5 ppm, based on the total weight of the curable composition, of complexed platinum metal, and

300 ppm, based on the total weight of the curable composition, of phenylbutynol as a catalyst inhibitor.

- The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Example 8

- 15 Silver particles with an average particle diameter not exceeding 1 micrometer, prepared by the reduction of silver nitrate, were ground in a ball mill using as lubricant a CarbitolTM acetate solution of a dimethylvinylsiloxo-endblocked polydimethylsiloxane exhibiting a viscosity of 100 centipoise (0.1 Pa.s) and containing 0.2 weight percent vinyl. Following the grinding operation, the excess dimethylpolysiloxane adhering on the surface of the silver particles was removed by washing the particles with xylene. This

- 20 yielded particles in the form of flakes with an average particle diameter of 4 micrometers.

A curable organosiloxane composition of the present invention was prepared by blending the following ingredients to homogeneity:

400 parts by weight of the silver particles

- 100 parts by weight of dimethylvinylsiloxo-endblocked polydimethylsiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and a vinyl content of 0.2 weight percent,

1 part by weight of a trimethylsiloxo-endblocked polymethylhydrogensiloxane with a viscosity of 30 centipoise (0.03 Pa.s) and a silicon-bonded hydrogen content of 1.5 weight percent,

a quantity of chloroplatinic acid/vinylsiloxane complex equivalent to 5 ppm, based on the weight of the curable composition, of complexed platinum metal, and

- 30 300 ppm, based on the total weight of the curable composition, of phenylbutynol as a catalyst inhibitor.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Comparative Example 4

- Silver particles with an average particle diameter not exceeding 3 micrometers, prepared by the reduction of silver nitrate, were ground in a ball mill using stearic acid as lubricant. Following the grinding operation the excess stearic acid adhering on the surface of the silver particles were removed by washing with xylene, which yielded particles in the form of flakes with an average particle diameter of 4 micrometers.

A curable organosiloxane composition outside the scope of the present invention was prepared by combining the following ingredients to homogeneity:

400 parts by weight of the silver flake

- 100 parts by weight of a dimethylvinylsiloxo-endblocked polydimethylsiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and a vinyl content of 0.2 weight percent,

1 part by weight of a trimethylsiloxo-endblocked polymethyl-hydrogen siloxane with a viscosity of 30 centipoise (0.03 Pa.s) and a silicon-bonded hydrogen content of 1.5 weight percent,

A quantity of a chloroplatinic acid/olefin complex equivalent to 5 ppm, based on the total weight of the curable composition, of complexed platinum metal, and

- 50 300 ppm, based on the weight of the curable composition, of phenylbutynol as a catalyst inhibitor.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 2.

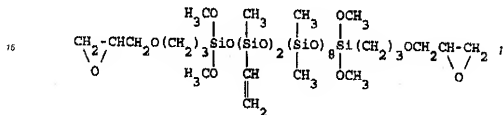
Example 9

Silver particles with diameters not exceeding 1 micrometer and prepared by the reduction of silver nitrate, were ground in a ball mill using vinyltrimethoxysilane as lubricant. Following the grinding operation

the excess vinyltrimethoxysilane adhering on the surface of the silver particles was removed by washing with xylene, which yielded silver flake with an average particle diameter of 2 micrometers.

A curable organosiloxane composition of the present invention was prepared by blending the following ingredients to homogeneity:

- 5 480 parts by weight of the silver flake particles
- 100 parts by weight of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and a vinyl content of 0.2 weight percent;
- 3 parts by weight of a trimethylsiloxy-endblocked polymethylhydrogensiloxane with a viscosity of 30 centipoise (0.03 Pa.s) and a silicon-bonded hydrogen content of 1.5 weight percent;
- 10 14 parts by weight of an organosilicon compound with the formula



a quantity of a chloroplatinic acid/vinylsiloxane complex equivalent to 10 ppm, based on the weight of the curable composition, of complexed platinum metal, and

400 ppm, based on the weight of the curable composition, of phenylbutynol as a catalyst inhibitor.

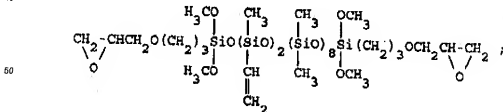
- 25 The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Comparative Example 5

- 30 Silver particles with an average particle diameter not exceeding 3 micrometer were prepared by the reduction of silver nitrate using hydrazine. These particles were ground in a ball mill using stearic acid as lubricant. Following grinding, the excess stearic acid adhering on the surface of the silver particles was removed by washing the particles with xylene. This produced particles in the form of flakes with an average diameter of 4 micrometers.

An electrically conductive silicone rubber composition was subsequently prepared by blending the following ingredients to homogeneity:

- 480 parts by weight of the silver flakes
- 100 parts by weight of a dimethylvinylsiloxy-endblocked polydimethylsiloxane with a viscosity of 2,000 centipoise (2 Pa.s) and containing 0.2 weight percent vinyl,
- 3 parts by weight of a trimethylsiloxy-endblocked polymethylhydrogensiloxane with a viscosity of 30 centipoise (0.03 Pa.s) and containing 1.5 weight percent of silicon-bonded hydrogen,
- 14 parts by weight of an organosilicon compound with the formula



a quantity of a chloroplatinic acid/vinylsiloxane complex sufficient to provide 10 ppm, based on the weight of the curable composition, of complexed platinum metal; and

400 ppm, based on the weight of the curable composition, of phenylbutynol as a catalyst inhibitor.

The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 2.

5 Example 10

A mixture containing 1) 25 weight percent of reduced silver particles with an average particle diameter not exceeding 2 micrometers and prepared by the reduction of silver nitrate using hydrazine and 2) 75 weight percent atomized silver particles with an average particle diameter not exceeding 2 micrometers
10 were ground in a ball mill using as lubricant a Carbitol™ acetate solution of a phenyl-containing silicone resin of Example 1.

Following the grinding operation, the excess silicone resin adhering on the surface of the silver particles was removed by washing with xylene, yielding particles in the form of flakes with an average diameter of 3 micrometers.

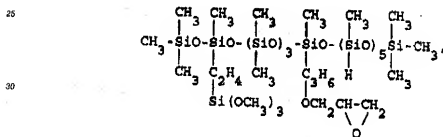
15 A curable organosiloxane composition of the present invention was prepared by blending the following ingredients to homogeneity:

450 weight parts of the silver particles

100 weight parts of a mixture of dimethylvinylsiloxy-terminated dimethylpolysiloxane and an or-
ganosiloxane resin containing the repeating units $(CH_3)_3SiO_{1/2}$ and $SiO_{4/2}$ the mixture exhibiting a viscosity
20 of 8,000 centipoise (8 Pa.s) and a vinyl content of 0.8 weight percent;

10 parts by weight of hydrophobized fume silica,

7 weight parts of an organosilicon compound with the formula



35 and a quantity of a microencapsulated chloroplatinic acid/vinylsiloxane complex equivalent to 10 ppm of platinum, based on the weight of the curable composition.

The catalyst was a dispersion of the chloroplatinic acid complex in a thermoplastic organosiloxane resin with a softening point of 80°C to 90°C.

40 The appearance and curability of the resultant curable composition together with the adhesion, contact resistance and volume resistivity of the elastomer prepared by curing the composition were evaluated and the results are reported in Table 1.

Table 1
Invention Examples

[illegible]

Table 2

Comparative Examples

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
5 <u>Untreated silver particles</u>	reduced silver	reduced silver	reduced silver	reduced silver	reduced silver
10 <u>Surface treating agent</u>	none	stearic acid	stearic acid	stearic acid	stearic acid
	<u>Silver particles after surface treatment</u>				
15 avg particle diameter (micrometers)	1	8	4	4	4
shape	granular	flake	flake	flake	flake
20 <u>Appearance of the silicone rubber compositions</u>					
initial	uniform	uniform	uniform	uniform	uniform
after 1 month	PS	PS	PS	PS	PS
after 3 months	PS	PS	PS	PS	PS
after 6 months	PS	PS	PS	PS	PS
25 <u>Hardness of the silicone rubber (JIS A)</u>					
initial	55	55	52	52	65
after 1 month	50	40	40	40	60
after 3 months	20	not cured	not cured	not cured	40
after 6 months	not cured	not cured	not cured	not cured	not
30 <u>Contact resistance of the silicone rubbers (ohm)</u>					
initial	2.0	0.6	0.4	0.4	0.4
after 100 hours	5.0	1.0	2.0	NM	1.0
after 500 hours	10.0	12.0	12.0	NM	11.2
after 1000 hours	15.0	20.0	18.0	NM	22.0
35 <u>Volume resistivity of the silicone rubbers (ohm-cm)</u>					
initial	4×10^{-4}	6×10^{-4}	5×10^{-4}	8×10^{-4}	8×10^{-4}
after 100 hours	4×10^{-4}	10×10^{-4}	15×10^{-4}	20×10^{-4}	9×10^{-4}
after 500 hours	10×10^{-4}	15×10^{-4}	50×10^{-4}	0.5	10×10^{-4}
after 1000 hours	20×10^{-4}	20×10^{-4}	80×10^{-4}	5.0	12×10^{-4}
40 adhesion of the silicone rubber	partial AP	partial AP	partial AP	AP	CP

NM=could not be measured PS=phase separation

Claims

1. An electrically conductive curable organosiloxane composition comprising the product obtained by blending to homogeneity
 - (A) 100 parts by weight of a first polyorganosiloxane containing at least two alkenyl radicals per molecule;
 - (B) an organohydrogensiloxane containing at least two silicon-bonded hydrogen atoms in each molecule, in a quantity sufficient to provide from 0.5 to 3 silicon-bonded hydrogen atoms per alkenyl radical in (A);
 - (C) from 50 to 2,000 parts by weight of finely divided silver particles treated with a first organosilicon compound selected from silanes containing at least one alkoxy group and organosiloxanes; and

(D) from one to 1,000 parts of a platinum group metal per one million parts of the combined weight of (A) and (B) of a hydrosilation catalyst to promote curing of said composition.

2. A composition according to claim 1 wherein said first organosilicon compound of (C) is selected from
5 silanes of the general formula $R_nSi(OR')_{3-n}$, cyclic organosiloxanes, a second polyorganosiloxane containing silanol groups on the terminal silicon atoms and organosiloxane resins wherein at least a portion of the repeating units are $SiO_{4/2}$ units, and wherein R and R' are individually selected from alkyl radicals containing from 1 to 4 carbon atoms.
- 10 3. A composition according to claim 2 wherein said composition further comprises up to 20 weight percent, based on the weight of said first polyorganosiloxane (A), of a second organosilicon compound containing at least one silicon-bonded alkoxy group per molecule.
- 15 4. A composition according to claim 3 wherein said second organosilicon compound further comprises at least one substituent selected from silicon bonded hydrogen, silicon-bonded vinyl, epoxy and trialkoxysilylalkyl.
5. A composition according to claim 3 where said organohydrogensiloxane (B) contains at least one
20 silicon-bonded alkoxy group.
6. A composition according to claim 1 wherein said silver particles are ground in the presence of said first organosilicon compound (C) as a lubricant.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 94115688.7

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D, A	US - A - 5 227 093 (COLE et al.) * Claims 1, 6 *	1
A	US - A - 5 015 413 (NAGAOKA) * Claim 1 *	1
		<p>CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)</p> <p>C 08 L 83/07 C 08 K 3/08 C 08 K 9/06 H 01 B 1/22</p>
		<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 6)</p> <p>C 08 L 83/00 C 08 K H 01 B</p>
The present search report has been drawn up for all claims		
VIENNA	05-12-1994	SEIRAFI
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>		